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Textural development of SiC and diamond wire sawed sc-silicon wafer

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Abstract

The present work compares the time-dependent evolution of the surface morphology during the horizontal acidic etching of diamond wire (DW) and SiC slurry (SP) sawn single-crystalline wafer by means of scanning electron microscopy (SEM), confocal microscopy, reflectivity measurements, and the measurement of the etch rates. Both sawing processes lead to different *as cut* structures which have a significant impact on the evolution of the wafer surface morphology during the acidic etching. This initial structure controls the sites where the chemical attack preferentially occurs and affects therefore to a considerable extent the morphology of the etched surface as well as the rate of which this morphology is formed. Based on the experimental results is discussed why the texturization of DW sawn wafers remains incomplete if acidic etch mixtures and etch parameters are used that were optimized for the etching of SP wafers. To create homogeneously texturized DW sawn wafers of low reflectivity the development of new etchants and new etch conditions for is necessary.

Keywords: texturisation; silicon wafer; slurry; diamond wire

1. Introduction

Diamond wire (DW) sawing of silicon bricks emerges as a serious alternative to the so far established multi-wire SiC slurry sawing process (SP). The DW process has numerous advantages, such as a higher productivity, a lower wear of the wire, and an easier recycling of the cooling liquid. However, both

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sawing processes lead to very different surface structures. The present work deals with the time-dependent development of the surface morphology (texture) of DW and SP sawn wafer by horizontal acidic etching. For this purpose SP and DW wafer were horizontally etched using a typical industrial etch mixture consisting of hydrofluoric acid (HF), nitric acid (HNO_3), and hexafluorosilicic acid (H_2SiF_6) [1]. The development of the texture is documented by the etch rate, the reflectivity as well as by inspection of the etched wafer surface with scanning electron microscopy (SEM) and confocal microscopy.

2. Experimentals

An industrial relevant acidic etching mixture was prepared from hydrofluoric acid (40% (w/w)), nitric acid (65% (w/w) both from Merck Darmstadt, Germany) and hexafluorosilicic acid (35% (w/w) from Alfa Aeser, Karlsruhe, Germany). Monocrystalline (100) silicon wafer with 15x15 mm diameter and 180-200 µm thickness were etched horizontally and simultaneously in the same beaker with varying time steps from 10 to 400 seconds at 10°C (Peter Huber Kältemaschinenbau GmbH Offenburg, refrigerated bath K12 + CC2). After etching the wafer were rinsed in water and dried. To follow the development of the etched surfaces the reflectivity was measured (Specord 250plus with integrating sphere from AnalytikJena AG), SEM pictures were taken as well as confocal microscopic measurements (µsurf solar from NanoFocus AG, Oberhausen) were performed.

The wafers were weighed before ($m_{as\ cut}$) and after (m_{etched}) etching with 0.1 mg accuracy. To compare the mass loss for different wafer the relative mass loss Δm_{rel} is used ($\Delta m_{rel} = (m_{as\ cut} - m_{etched}) / m_{as\ cut}$). From Δm the etch rate r ($r = \Delta d/t$) is calculated using the density of silicon (ς_{Si}), the area of the etched wafer slice (A_{wafer}), the thickness loss Δd ($\Delta d = \Delta m / (\varsigma_{Si} * A_{wafer})$), and t etch time without the induction period.

3. Results and discussion

3.1. As cut wafer surface

Already the visual inspection of the two wafer types reveals their differences. The SP wafers have a regular grey appearance in contrast to the DW wafer with a silver shiny surface and clearly visible parallel grooves.

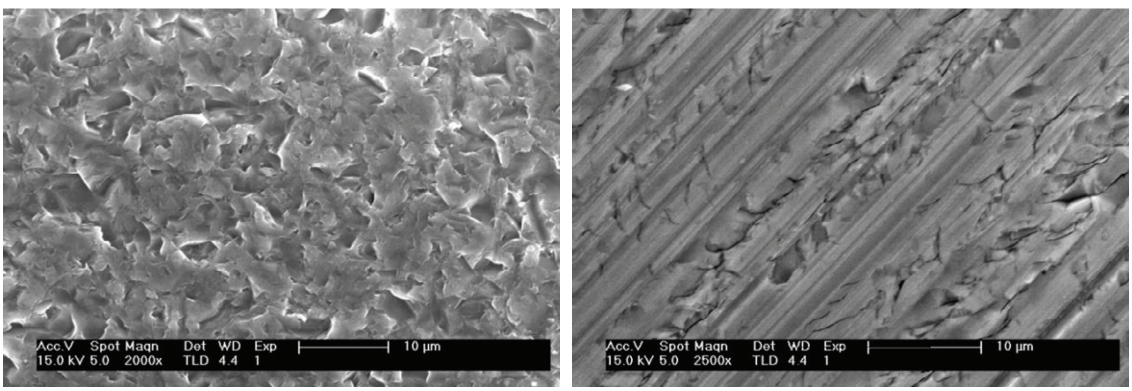

Fig.1. SEM micrographs of the *as cut* SP (left) and DW (right) sawn wafer surfaces

The SEM micrographs in Fig. 1 show these significant differences between the surfaces of the slurry

(SP) and the diamond wire (DW) sawn wafers in detail. The slurry sawn surface is characterized by a homogeneously distributed rough, dentate, fractured surface. In contrast, the diamond wire sawn wafer features smooth parts, parallel rifts, individual fractures, and areas of cracks along the rifts. The initial reflectance of DW wafer is typically around 26% and always higher than for the SP wafers with typical values about 24%. These smooth regions of the DW sawn wafer might be considered as the reason for the higher reflectivity values for the DW wafer.

3.2. Etch rate

The impact of the surface structure on the etch rate was studied as first step. The normalized mass differences caused by the dissolution of silicon in Fig. 2 reveal that the SP and DW wafer behave very similarly in the etching process. The derived etch rates show the same behavior. Only the initial etch rate of the DW wafer is slightly higher than for the SP wafer. Both etch rates drop clearly in the first 50 seconds. Above 100 seconds the etch rates of both wafer types approach a uniform level which is observes when the saw damage is removed and the bulk silicon is etched [1].

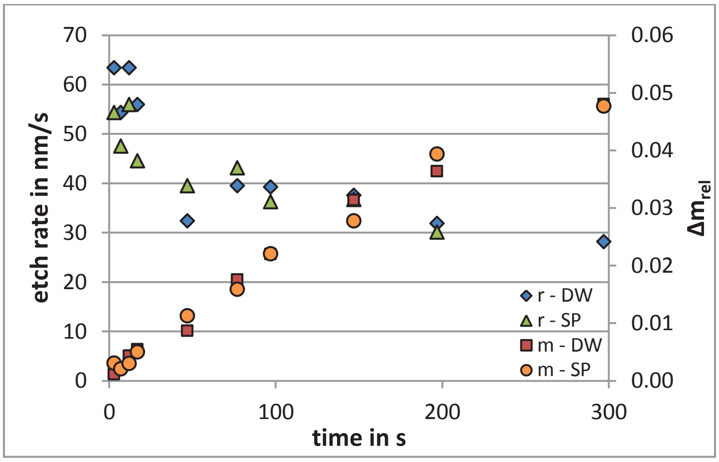

Fig. 2. Etch rate (r) and relative mass loss (Δm_{rel}) of etched SP and DW wafer as function of the etch time

3.3. Reflectivity and SEM micrographs

The plot of the reflection differences ΔR ($\Delta R = R_{as\ cut} - R_{texture}$) vs. the loss of thickness (Δd) in Fig. 3 exhibits significant differences between both wafer types. For the SP wafer ΔR decreases with etching and reaches a shallow minimum at an etch depth close to 2 µm. The highest value of the reflection difference is about -7%. However, at this point the saw damage of the SP wafer is not yet removed. Above 2 µm ΔR shows a shallow increase with the etch time that persists even if the wafer is etched further than the depth of the saw damage of approx. 5 µm. As expected, as longer the etch time as smoother the surface and as higher the reflectance.

In case of the DW wafer the reflection difference ΔR decreases strongly and reaches its minimum at an etch depth around 1 µm. The maximum of ΔR is about -11%. After the minimum has passed ΔR increases steeply up to a value of - 4%. Finally, for an etch depth of more than 3 µm ΔR increases linearly with the etch depth.

For the SP wafer the development of ΔR as function of the etch depth can be explained with the help of the micrographs shown in Fig. 4. After 10 seconds of etching almost no difference is observed between the *as cut* structures of both wafers (c.f. Fig. 1). However, this short etching causes the observed initial drop in ΔR (Fig. 3). Recently it had been shown that already a short etching is sufficiently to remove the topmost layer of silicon or silicon debris that hides small rifts and cracks [1]. With increasing etch time a randomly distributed rift-valley-structure is formed. Finally, these valley-like structures are broadened with longer etch time leading to the steadily increasing values of ΔR.

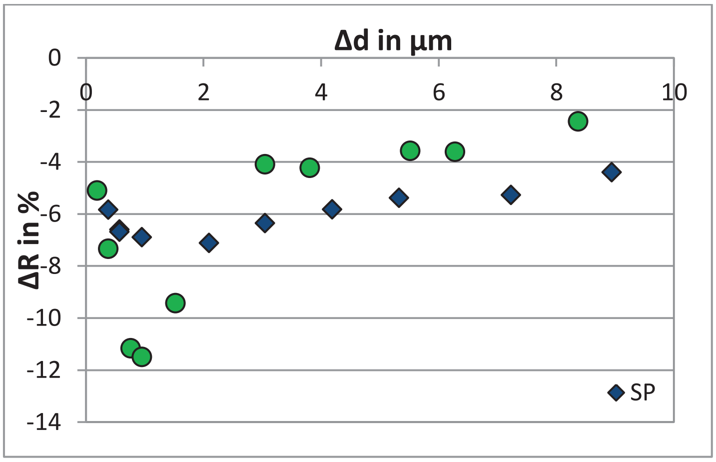

Fig. 3. Change of reflection ($\Delta R=R_{as\ cut}-R_{texture}$) as function of the thickness loss (Δd) for etched SP and DW wafer

In contrast, the 10 seconds etching of the DW wafer the SEM micrograph shows no significant progress compared to the *as cut* structure. The inspection by confocal microscopy makes clear a similar behavior to the SP sawn wafer: The removal of the topmost silicon layer or silicon debris reveals hidden structural details. Additionally, a preferential attack at the fracture cracks leads to deeper cracks and valleys. Both cause presumably the initial drop of ΔR. After 80 seconds the fractured areas have turned into texturized areas and a beginning texturization along the sawing rifts is observed. However, a considerable fraction of the surface and even some parts of the rifts appear unaffected in the SEM micrographs. The inspection by confocal microscopy indicates that the apparently smooth areas are attacked by the etchant and that etch pits are generated on these areas and on the majority of the rifts. With ongoing etching these pits turns into valleys and the rift structures disappear more and more. After 300 seconds of etching the texturization covers now a wider area of the wafer surface. However, the rift-like structures are still recognizable.

The interpretation of the ΔR curve after the minimum is more difficult for the DW sawn wafer. The micrographs suggest that the preferential etching of the crack areas (i.e. at the bottom of the large, fractured valleys) leads to a smooth surface at the bottom of these valleys for a quite short etching time. The steep increase of ΔR is attributed to the increased reflection of light from these valleys with smooth and flat bottom.

It becomes very clear that the DW sawing process generates an inhomogeneous silicon surface that exhibits areas of a very distinguished reactivity against the acidic etchant. In principle, these results confirm the findings of Bidiville et al. [2] made for DW wafer. They explained these differences with amorphous silicon that was found on the diamond wire cut wafer and act as an etching mask compared to the slurry wafer without amorphous silicon on the surface.

Finally it should be noted that the absolute reflectivity of the etched DW wafer is always higher than for the SP wafer. The reason is seen in the etched structure of the DW wafer that is plainer than those of the texturized SP wafer.

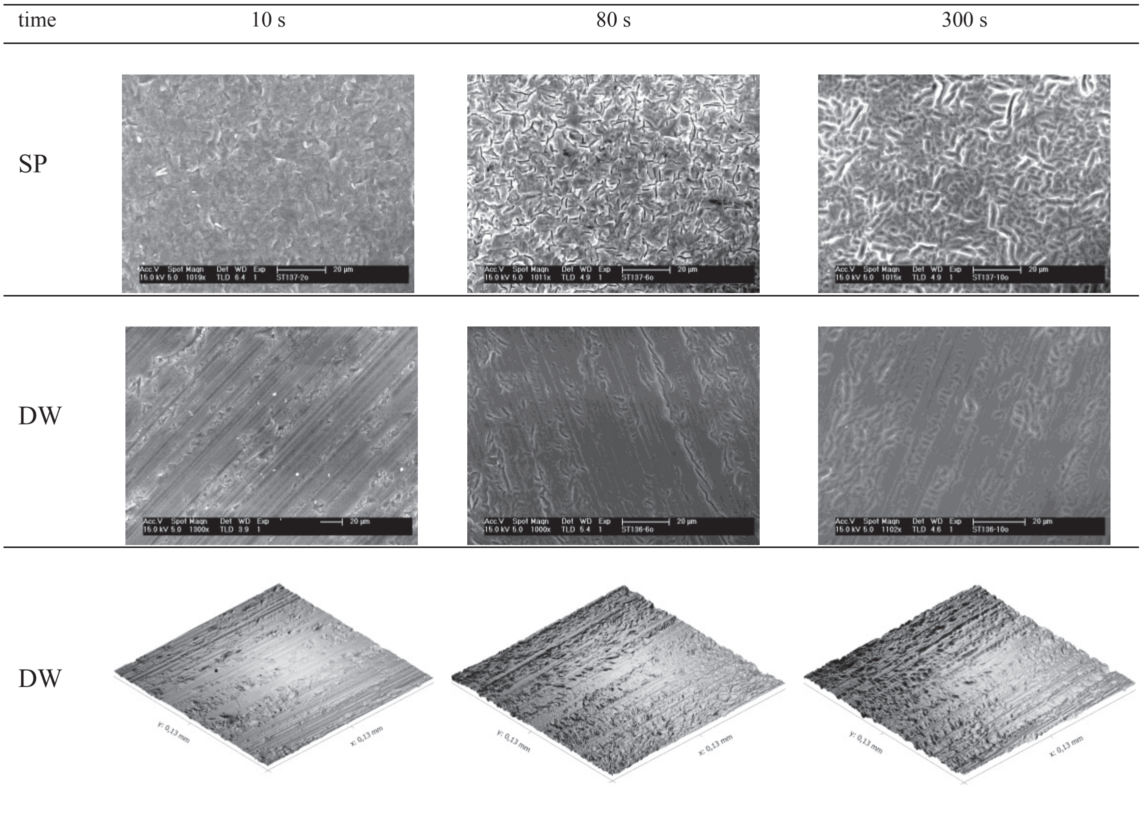

Fig. 4. Micrographs made by SEM and confocal microscopy from the etched surfaces of SP and DW sawn wafers after different etch times

3.4. Surface evaluation

The 3D-analysis of the etched wafer surfaces gives an insight into the importance of the *as cut* surface structure on the development of the morphology in the etch process. The surface area to projected area ratio (Fig. 5) reveals a constant offset between the SP and DW curve. That means that the diamond wire cut wafer possesses initially and throughout the entire etch process a lesser surface area than the SP sawn wafer. It appears that an initially formed surface structure formed by the sawing process cannot be changed by the applied etching process.

Remarkably, the curves for the two differently sawn wafers in Fig. 5 proceed almost parallel. The initial drop of the plotted surface parameter describes an enlargement of the surface area due to etching. In case of the SP wafer this corresponds to the removal of the topmost layer and the uncovering of rift and crack structures [1]. At the curve maximum between 50 and 100 seconds the saw damage is almost completely removed. The almost constant etch rate (Fig. 2) and the decrease of the surface parameter at higher etch times indicate that the etching process now attacks undisturbed bulk silicon leading to broader and shallower surface structures to that the absolute reflectivity increases i.e. ΔR decreases (Fig. 4). At this time a sound interpretation for the curve of the DW wafer can not be given, however, it can be assumed that the ongoing processes are similar to that discussed for the SP wafer.

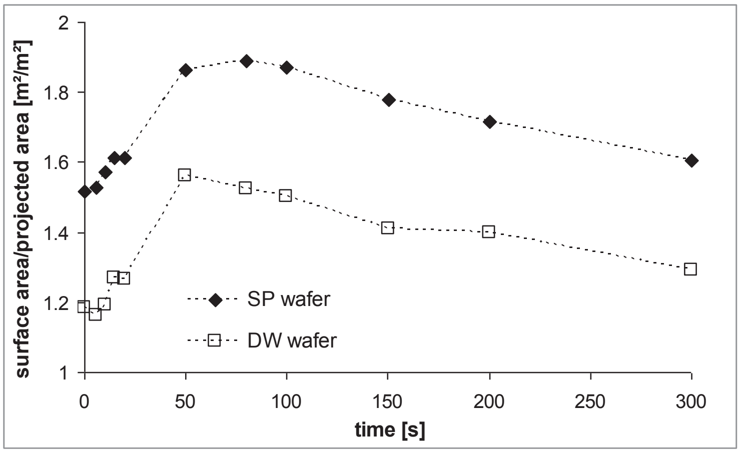

Fig. 5. Change in the ratio of the surface area to the projected area as a function of the etch time

4. Conclusion

The presented results show very clearly that the wafer sawing process is of essential importance for the acidic etching step that generates the required surface texture for an efficient harvesting of light. The wafer sawing process produces an *as cut* surface morphology that behaves like a mask during the etching. This mask controls the sites where the chemical attack preferentially occurs. Furthermore, it controls to a considerable extent the morphology of the etched surface and the rate of which this morphology is formed. Moreover, it might be concluded that the specific features of the mask introduced initially by the wafer sawing process can not be changed in the etching process. Remarkably, the total etch rate seems to be unaffected by the *as cut* structure. Obviously, etch mixtures and etch parameters (e.g. etch time, temperature) optimized for the etching of DW saw wafers are not suitable for a successful texturization of DW sawn wafers. This requires the development of new etch mixtures and new etch parameters to achieve a fast and uniform texturization of DW sawn wafer. However, such changes might have an enormous impact on any other parameters, e.g. on the utilization of the used acids (stoichiometry of etching) [3], on the nature and composition of the gaseous reaction products as well as on the nature and concentration of the reactive intermediates that are enriched in the etchant.

Acknowledgment

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